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## Meeting Log

Subject: Meeting with Ted Williams et al., concerning completed and future activities by the Gas Research Institute/Mosaic Industries in the area of CO detector test protocol development/implementation.

Meeting Date: May 14, 1996

Place of Meeting: CPSC, East-West Towers, Room 612

Date of Entry: May 15, 1996

Source of entry: Tim Johnson, ESEE

### Commission Attendees:


Tim Johnson, ESEE  
Elizabeth Leland, EC  
Laureen Burton, EH

### Non-Commission Attendees:

Ted Williams, Gas Research Institute (GRI)  
Dr. Paul K. Clifford, Mosaic Industries, Inc.  
Michael A. Brown, McCutchen, Doyle, Brown, and Enersen  
Eric Titland, Quantum Group, Inc.  
Alex Cohen, concerned citizen/consumer  
Sandy Ruiter, Underwriters Laboratories (UL)  
Maureen Ciso, Product Safety Letter

### Summary of Meeting:

The meeting was requested by Mr. Ted Williams, GRI. Mr. Williams and Dr. Paul Clifford, Mosaic Industries, discussed current GRI activities in the area of test protocol development for CO detectors. The meeting then centered around a discussion of both completed and planned activities GRI is involved with. The eventual goal of these activities would be to develop a test protocol, methodology, set-up etc. that could be adopted by any nationally recognized testing lab such that uniform test methods/ test results could be implemented/achieved by all laboratories. Both Mr. Williams and Dr. Clifford stressed that they are seeking comments on the DRAFT test protocol (GRI DRAFT Topical Report titled: Test Protocols for Residential Carbon Monoxide Alarms, Phase 1) that has been put forth by GRI/Mosaic Industries. They are seeking input from anyone interested in participating (helping fund or provide input into) in this test protocol development process.



## Discussion:

Five handouts were distributed by various meeting participants and are attached to this meeting log. They are:

- 1) 1 page article from American Gas Magazine titled: A.G.A. Calls British Report on Gas Stoves 'Flawed'
- 2) 1 page handout, subject: CO Detection Level Comments from Quantum Group, Inc.
- 3) 13 page handout titled: Technical Proposal: Performance Testing of Residential CO Detectors, dated May 3, 1996
- 4) 21 page handout, titled: Test Protocols for Carbon Monoxide Alarms Phase I
- 5) 4 page handout titled: CO Detector Testing: Discussion With Consumer Product Safety Commission, dated May 14, 1996

In addition two GRI Topical Reports are mentioned below and were discussed in the meeting. These reports are not attached but should be available from GRI. These reports are:

- 1) GRI Topical Report, titled: Carbon Monoxide Alarm Performance Testing Phase I: Basic Performance Task 1: Steady-State CO Concentration Tests (report number GRI-95/0220).
- 2) GRI DRAFT Topical Report titled: Test Protocols for Residential Carbon Monoxide Alarms, Phase 1 (report number GRI-96/0055).

Ted Williams began by giving a general overview of completed and future GRI activities. He mentioned that GRI has completed basic performance tests on CO detectors (GRI Topical Report titled: Carbon Monoxide Alarm Performance Testing Phase I: Basic Performance; Task 1: Steady-State CO Concentration Tests). Further, phase 1 test protocol development has been completed (GRI DRAFT Topical Report titled: Test Protocols for Residential Carbon Monoxide Alarms, Phase 1). Comments are welcome on the draft report but if possible should be submitted to GRI or Mosaic before June 1.

Mr. Williams then explained some future activities. First, GRI is considering trying to organize an ASTM task force dealing with testing of CO sensor systems. Second, some tests will be run on CO detectors from the new test protocol developed by GRI - a phase II demonstration phase. The goal would NOT be to judge specific detector performance but rather to demonstrate feasibility of implementing the test protocol. It was mentioned that some gas utilities are interested in participating and that GRI is looking for other interested parties to participate as well. A third activity may involve development of a new technical specification for CO detectors, possibly implemented through the International Approval Service (IAS)/American Gas Association (AGA). The specification would seek to improve quality control for CO detectors. See attached handout titled: CO Detector Testing Discussion with Consumer Product Safety Commission.

Dr. Paul Clifford continued the presentation by explaining in more detail the phase 1 DRAFT report mentioned above. See attached handout titled: Test Protocols for Carbon Monoxide Alarms, Phase 1.

Finally, it was mentioned that GRI/Mosaic have developed a technical proposal for performance testing of residential CO detectors and are looking for interested parties/funding to participate in this performance testing effort. See attached handout titled: Technical Proposal: Performance Testing of Residential CO Detectors.

attachments (5)



THE MONTHLY MAGAZINE OF THE  
AMERICAN GAS ASSOCIATION

Volume 78, No. 4 • May 1996

## A.G.A. Calls British Report on Gas Stoves 'Flawed'

A.G.A. says it has identified serious flaws in a recent report in the British journal *Lancet*, which claimed that women who cook on gas ranges are more likely to suffer from asthma-like symptoms.

The report, according to A.G.A., relied on data collected from an unscientific survey of men and women who cook on unvented gas ranges and who also report health problems, such as asthma. A.G.A. says the methodology in that survey does not support a scientific correlation between the two situations. In addition, as noted in the *Lancet* report, other studies on this general topic — which have focused on emissions of nitrogen dioxide ( $\text{NO}_2$ ) — have been inconclusive and contradictory.

In a 1981 staff paper, the U.S. Environmental Protection Agency (EPA) found “little credible evidence” linking specific human-health effects to short-term exposures to nitrogen oxides ( $\text{NO}_x$ ), which includes the collective emissions of nitric oxide and  $\text{NO}_2$ .

The average long-term (more than 24 hours) concentration of  $\text{NO}_2$  in kitchens with unvented gas stoves generally ranges between 0.03 and 0.08 parts per million (ppm), with one-hour peaks falling in the 0.15- to 0.3-ppm range. The EPA report went on to say that “no rigorous rationale” was found for setting a specific indoor air-quality standard for  $\text{NO}_2$ .

When natural gas is burned, says A.G.A., the primary byproducts are water vapor and carbon dioxide — the same substances that are exhaled when people breathe. “Combustion of natural gas can produce trace amounts of some other substances, including  $\text{NO}_x$ , but it is virtually impossible for toxic levels to be emitted if appliances and equipment are installed and operating properly and are used properly,” insists the association.

May 14, 1996

**Subject: CO Detection Level Comments from Quantum Group, Inc.**

- Our sensors are working as designed to detect above 20 ppm CO. Such a sensor is needed to protect people's health and safety.
- UL and our studies have not found Quantum sensors to be responding to interference gases.
- We can make our sensors less sensitive to CO in a manner similar to those we sell in Japan. They respond above 50 ppm; we have also developed a 35 ppm threshold sensor which will be field tested starting in July.
- We recommend an extensive indoor air quality (contamination gases) survey of homes before considering a standard's modification. That survey should identify potential interference gases and determine those levels in people's homes. Further, and most importantly, the survey should consider the health effects of the gases and their source.

Erik Titland  
Quantum Group, Inc.  
11211 Sorrento Valley Road  
San Diego, CA 92121

**Technical Proposal:**  
**Performance Testing of Residential CO Detectors**

To:

**Gas Research Institute  
8600 West Bryn Mawr Avenue  
Chicago, IL 60631**

Submitted by:

**Dr. Paul K. Clifford  
and  
Dr. Michael G. Dorman**

**Mosaic Industries, Inc.  
5437 Central Ave., Suite 1  
Newark, CA 94560  
510-790-8222**

**May 3, 1996**

**For evaluation purposes only, by or on behalf of GRI**

# Performance Testing of Residential CO Detectors

## Executive Summary

There is a rapidly growing market for residential wall mount alarms that detect hazardous gases such as carbon monoxide (CO). The availability of low cost alarms and their associated marketing have generated sales of millions of units nationwide, and the trend is accelerating. It has become apparent to many interested parties that there is a national need for more thorough testing of these widely used detectors. A detailed testing protocol has been developed for GRI by Mosaic Industries to supplement the tests in the Underwriter's Laboratory (UL) CO standard<sup>1</sup>. The proposed protocol includes tests of a detector's sensitivity to carbon monoxide gas, a test for the distribution of sensitivity among detectors, tests for interference-gas-induced false negatives and false positives (false alarms), a test of detector repeatability, and accelerated lifetime exposure tests. Implementing these rigorous tests should lead to assurance of higher reliability in mass marketed CO alarm instruments.

As explained later in this document, the design of more sophisticated gas delivery equipment is required to perform all of the comprehensive tests in the proposed protocol on the large number of detectors required to establish statistically significant measures of reliability. Mosaic Industries has developed new approaches to gas delivery that could be applied to the development of this advanced equipment in a future project. However, much useful information can be gained now by performing key portions of the CO test protocol on small batches of detectors using presently available gas delivery equipment. Performing these well chosen tests would greatly increase the available data about commercially available CO detectors, and would provide an objective basis for performance assessments.

Mosaic Industries maintains state-of-the-art dynamic gas delivery and response characterization facilities in its laboratories. These facilities comprise a pure air system, a computer-controlled humidification apparatus capable of delivering relative humidities from under 5% to over 80%, multi-channel gas and solvent delivery modules, an 80 liter test chamber, and an operator console that controls the gas delivery system. Unlike the "static" gas systems typically used to implement detector testing, the computer-controlled dynamic gas delivery equipment continuously mixes the target gases and vapors to achieve well controlled concentrations, high gas purity, and excellent experimental repeatability.

The gas delivery facilities at Mosaic Industries are capable of delivering CO and interferents to batches of ten detectors at a time. After customizing a data acquisition module to acquire data from the specified alarm instruments, the gas delivery system can be programmed to perform the specified tests. These include tests of the alarm level to verify compliance with the UL 2034 standard for CO sensitivity, as well as tests of low concentration immunity, transient concentration immunity, repeatability, and interfering gases. An analysis of the resulting performance data will provide an objective basis for assessing the capabilities of the CO alarms.

A number of organizations including GRI and several gas utilities have expressed interest in participating in such a CO testing project. We propose that the project be structured as a consortium in which GRI is the primary participant that supports the non-recurring testing costs (such as the initial customization of the data acquisition apparatus), and each additional participant selects a batch of up to 10 detectors for testing and supports the costs of testing this batch. A final report will provide a quantitative summary of the test results from all of the tested detectors. This consortium structure shares the testing costs among all of the participants and GRI, and provides an efficient means of testing a variety of residential CO alarms.

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<sup>1</sup> See the draft final report titled "A Test Protocol for Residential Carbon Monoxide Alarms, Phase 1".

# **Performance Testing of Residential CO Detectors**

## **Background**

The installed base of residential wall-mount CO alarms is growing rapidly in the United States. Several factors are responsible for their sudden popularity: the new availability of low cost CO detectors and their nationwide marketing, the adoption in 1992 of an Underwriters Laboratories Standard (UL 2034) for their performance, publicity campaigns by the American Lung Association, and the advocacy of the US Consumer Products Safety Commission (CPSC). There has also been an increased public and media awareness of the dangers of CO. The first municipal regulation requiring CO detectors was written by the city of Chicago. In October 1994, the city began requiring detectors in most residential and certain public buildings located within the city's limits. Other city administrations are watching the Chicago experience closely, although none are currently considering detector mandates. Although current market data is scant, it is estimated that there are between 7 and 8 million units installed as of January 1996, and market penetration is expected to grow to tens of millions of units within several years.

### **Increasing Calls to Utilities and Fire Departments**

The increased awareness of the dangers of CO has resulted in increased service calls to utilities and heating contractors. Moreover, as detector installation has grown over the past two years there have also been an increasing number of calls to authorities from consumers whose detectors have sounded an alarm. While some of these calls may represent responses to dangerous levels of CO, in addition there are undoubtedly many other false alarms. In fact, false alarms in the city of Chicago have become such a problem that some have recommended overturning the city's detector mandate.

With the increasing prevalence of CO detectors other cities are beginning to report similar experiences. In Los Angeles there were more than 3,300 nuisance alarms during the month of November 1995. This was more than 100 times the false alarm incidence of prior months. As in the Chicago incident, this surge of alarms apparently resulted from an annual winter-long thermal inversion layer trapping low levels of CO close to the ground. Many of these false alarms required an emergency response from both local fire departments and the gas utility. The Southern California Gas Company reportedly logged 2,500 such responses in November alone. The dependence of the day-to-day alarm rate on meteorological conditions in both Chicago and Los Angeles strongly suggests that the majority of alarm incidents are not caused by dangerous CO concentrations but rather that they are false alarms caused by low ambient CO levels.



### The Costs of Inadequate Detector Performance

The costs of false alarms are significant. These costs are generally not borne by the detector manufacturers but instead they are imposed on the various responders to the alarm including fire departments and utilities. The cumulative costs of false alarms have not been compiled but they are undoubtedly great. For example, fire departments in suburban Chicago expend approximately one vehicle hour per false alarm, and gas utilities estimate that service calls cost approximately \$250 per call. If we assume this rate as a minimum bound on the response cost, then during just the first three months of the Chicago regulation requiring detector installation, the cost of false alarms in Chicago was more than two million dollars.

A less tangible cost of false alarms results from a consumer's lack of confidence in the detector. After a false alarm many consumers may disable their detectors so that they are no longer protected, or, worst yet, tired of a detector that "cried wolf" too many times, they may ignore future alarms.

False negatives may be an even greater problem even though they cause no immediate response cost. False negatives result when an alarm fails to sound even when exposed to dangerous levels of CO. Because they can not be detected by the consumer there may be many consumers who are not protected by their detectors while being given a false sense of security.

### Apparent Problems with the UL 2034 Standard

The widely accepted means to assure the quality of CO detectors is to require their certification to a common standard for performance. The Underwriters Laboratory (UL) has offered consumers an important service by developing such a standard. The standard specifies the detectors' required CO sensitivity with the goal of ensuring that the physiologically important carboxyhemoglobin level be limited to less than 10%. The UL assessments of performance parameters that are not directly related to the detectors' gas sensing function (for example those related to electrical properties, power supply safety, stability with respect to short term temperature and humidity variation, and durability during shipping) are quite thorough. Since the UL developed performance standard No. 2034 for residential CO detectors, many manufacturers have had their products certified by the UL.

Yet problems persist despite the certification of these alarms by the UL standard. For example, it appears that the original UL 2034 did not anticipate false alarms resulting from long term exposure to low concentrations of CO. One drawback of cumulative-response sensors may be that they are not fully reversible when exposed to low concentrations of CO for long periods of time. On subsequent exposure to greater concentrations they have a lower alarm threshold than they should, and in the worst case they may simply false alarm after sufficient time at ambient concentrations. Because the standard did not anticipate false alarms from a sufficiently long-term exposure, there were no tests in the original standard that would detect this failure mechanism. A recent revision addresses this problem, but false alarms at ambient CO levels apparently still persist.

It also appears that the present standard does not sufficiently anticipate failures that may result from the individual weaknesses of various sensing technologies that may be employed in the detectors. These technologies, colorimetric sensors, semiconductor sensors, catalytic beads, electrochemical cells, and infrared detection, have response mechanisms with widely differing behaviors that should be probed using a variety of challenges as described in the comprehensive CO Test Protocol Report prepared by the contractor for GRI<sup>1</sup>.

### **Motivation and Benefits**

Owing to the increasing consumer concern about CO, the rapidly growing installation of CO detectors, and the concomitant rise in nuisance alarms and calls to utilities, many in the gas industry have expressed an interest in the testing of residential CO detectors. Some utilities want to ascertain which commercially available detectors are the most reliable so that they can recommend the appropriate detectors to customers, or sell the detectors as a service to their customer base. Others want to gather technically sound experimental data to judge the performance of detectors that are commercially available now or that will be introduced in the near future. All of these perspectives and interests suggest that a well conceived testing program should be undertaken to evaluate representative residential CO detectors.

A cost effective and timely testing project can be undertaken now using presently available automated gas delivery equipment at Mosaic Industries. The proposed tests would apply a subset of the tests proposed in the comprehensive CO Test Protocol Report<sup>1</sup>, including tests of the alarm level to verify compliance with the UL 2034 standard for CO sensitivity, as well as tests of low concentration immunity, transient concentration immunity, repeatability, and interfering gases.

An analysis of the resulting performance data will provide data to evaluate the short-term performance of the detectors, establish their basic functionality, and verify their adherence to the UL 2034 standards for CO sensitivity. In short, it will provide an objective basis for assessing the capabilities of residential CO alarms.

In recognition of the fact that GRI and a number of other organizations are interested in CO detector testing, we propose that the project be structured as a consortium. With GRI as the primary participant that supports the non-recurring testing costs (such as the initial customization of the data acquisition apparatus), each additional participant selects a batch of up to 10 detectors for testing and supports the costs of testing this batch. A final report will provide a quantitative summary of the test results from all of the tested detectors. This consortium structure shares the testing costs among all of the participants and GRI, and provides an efficient means of testing a variety of residential CO alarms.

In addition to providing timely and relevant performance information, this testing program would be a first step towards a comprehensive testing program that evaluates hundreds of each type of detector to establish statistical measures of reliability as described in the CO Test Protocol Report<sup>1</sup>.

## Technical Approach

The proposed tests will be performed in the laboratories of Mosaic Industries using the automated gas delivery and characterization equipment described in the "Test Facilities" section below. The following set of five tests will be performed to provide an objective basis for assessing the performance of the instruments under test.

### Alarm Level Test

The alarm actuation levels should be tested in accordance with UL 2034, except that at the 100 ppm (parts per million) level the alarm must not sound within 15 minutes (UL 2034 specified 5 minutes) as explained in Chapter 6 of the CO Test Protocol Report<sup>1</sup>. Detectors that pass this more stringent requirement are less likely to false alarm at non-hazardous levels of CO. These tests require that the detector alarm within the following times:

- Within 90 minutes, but not less than 15 minutes, for CO concentrations of 100 +/-5 ppm.
- Within 35 minutes for CO concentrations of 200 +/-10 ppm.
- Within 15 minutes for CO concentrations of 400 +/-20 ppm.

These tests are to be performed at 23° +/-3°C and at a relative humidity of 50 +/-20% after a minimum of three hours conditioning time at this temperature and humidity. During each gas exposure the time to alarm will be measured for each instrument under test in order to estimate the distribution of sensitivities among detectors. The variance and distribution of the alarm level, expressed as cumulative exposure time to alarm, will be measured at each gas level.

### Immunity to Low Concentrations Test

The detectors will be exposed to 20 ppm CO for 10 days continuously and the time to alarm, if indeed there are any alarms, will be measured.

### Surge Immunity Test

The detectors will be tested for immunity to transient CO levels that are significantly greater than those expected in ambient air but that are still a large factor less than hazardous. Excursions of up to 50 ppm for one half of an hour can occur during rare incidents of backdraft or with infiltration of automobile traffic exhaust. Yet 50 ppm for 30 minutes causes a carboxyhemoglobin level of less than 2.5%. During this test the detectors will be exposed to 50 ppm for 30 minutes. Total accumulated exposure per test should be 1500 ppm-min +/- 150 ppm-min.

### Repeatability Test

Detectors should be capable of repeated alarming so that they reliably alarm on acute exposure even if in the past they had already experienced one or more alarm incidents. Unlike the UL 2034 test which allows sensor replacement after each gas exposure of the gas sensitivity test, the three exposures of the Alarm Level Test should be applied to the same detector instrument, but with a recovery period in clean air of 24 hours between exposures. After each exposure those detectors capable of a manual reset should be reset. Those detectors which reset automatically should do so within the specified recovery time after the removal of gas. Still using the same instrument, the triple exposure Alarm Level Test should be performed twice more. For each exposure the time to alarm will be measured and any trend to greater or lesser sensitivities throughout the tests will be noted.

### Interfering Gas Test

Detectors should be exposed to significant concentrations of various potentially interfering gases, each for a duration of two hours. Gas types and concentrations are tentatively chosen as follows:

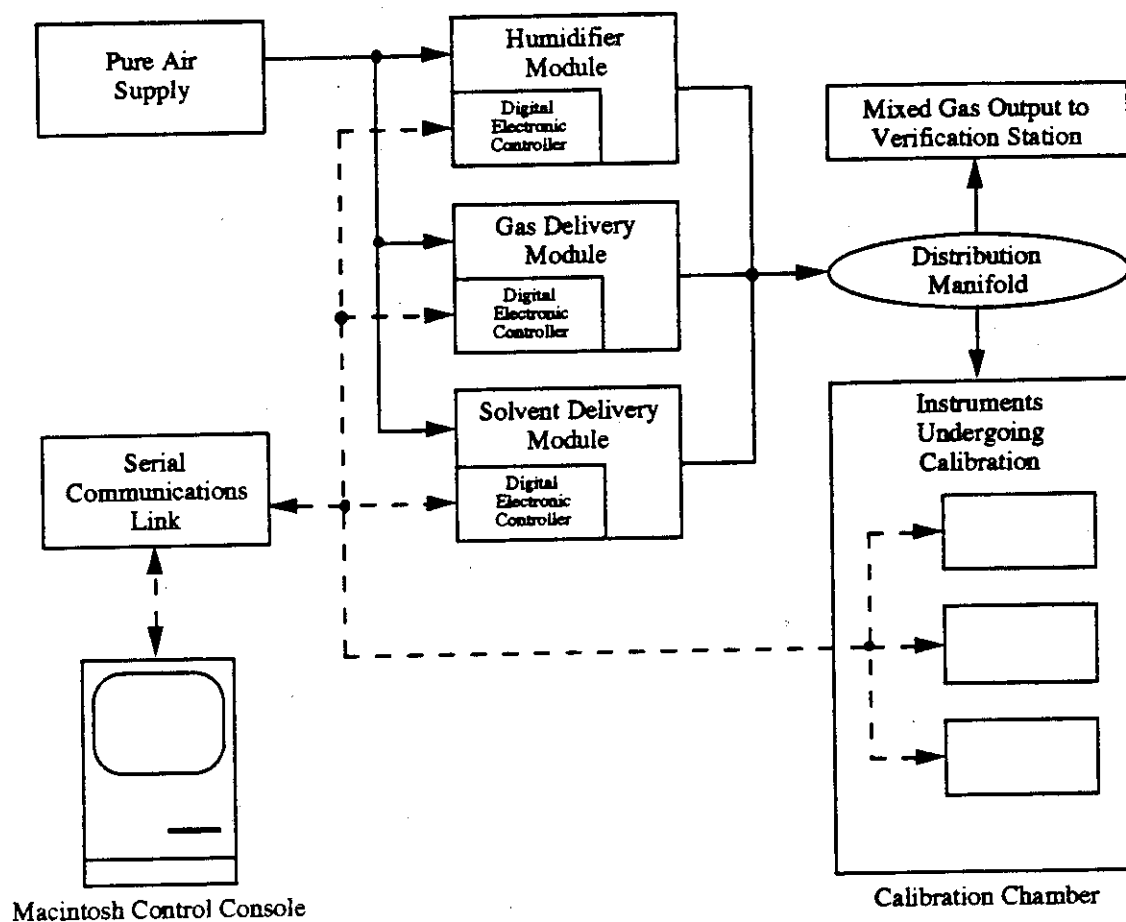
Ammonia	100 ppm
Acetone	200 ppm
Ethylene	200 ppm
Ethanol	200 ppm
Heptane	500 ppm
Isopropyl Alcohol	200 ppm
Toluene	200 ppm
Ethyl Acetate	200 ppm
Trichloroethane	200 ppm

The time to alarm, if there are any alarms, will be measured to determine the susceptibility to false alarms.

## **Test Facilities**

The automated gas delivery system developed by Mosaic Industries is capable of accurately delivering mixtures of CO and interfering gases and vapors over wide concentration ranges in a pure air carrier stream with controlled relative humidity. An on-line gas chromatograph (GC) facilitates verification of gas delivery during testing.

Figure 1 presents a high level view of the automated test station. An Apple Macintosh control console runs a spreadsheet-style graphical user interface and control program that allows rapid specification of automated test protocols. The console also coordinates the activities of constituent modules by communicating with the embedded digital controllers in each module. An air supply delivers dry air to a humidifier, a dynamic gas delivery module, and a dynamic solvent delivery module. The mixed gas output is delivered to a detector chamber for the testing of multiple gas detection units.



**Figure 1.** Overview of the automated gas delivery and testing station.

Because the sensors being tested modify the surrounding gas ambient by catalyzing the oxidation of some gases, a dynamic flow of at least ten liters per minute into the test chamber must be delivered to assure stable, well controlled concentrations. "Static" gas systems that establish concentrations via simple gas injection into a fixed volume often lead to poor experimental reproducibility as the test gases are burned by the sensors and absorbed and later released by the interior surfaces of the test chamber. A dynamic system avoids these problems by maintaining a constant flow of freshly mixed gases through the test chamber to ensure reliable assessment of performance.

A solvent module delivers up to 8 simultaneous species of solvent vapors. Air flow control and humidification modules control up to twenty liters per minute of pure air with relative humidity ranging from approximately 1% to over 80%.

The following subsections describe each component of the test station in detail.

## Pure Air System

In order to characterize the response of sensors and detectors to trace quantities of gases and vapors, we must start with air that is free of impurities and then add well-known amounts of the target gases and vapors. The pure air system provides a cost-effective conversion of room air to pure dry air for use in the test facility.

Room air is compressed to 125 psig (pounds per square inch above atmospheric pressure) by an oil-less compressor and then cooled by passing the air through a radiative cooler. Liquid water generated by the compressing and cooling of the air is removed with a coalescing filter. The air is thoroughly dried with a heatless dryer, passed through a second coalescing filter and stored in a 30 gallon tank.

The compressed air is purified as it passes through both desiccant and a breathing-air filter containing activated alumina desiccant, activated charcoal and a room-temperature catalyst bed that removes organic contaminants as well as some simple inorganics such as hydrogen sulfide and ambient CO. A heated catalyst bed oxidizes trace quantities of methane, sulfur compounds, hydrogen, and other reducing gases. A downstream desiccant removes water vapor generated by the oxidation in the catalyst bed, and an activated charcoal filter removes any oxides of nitrogen produced in the catalyst bed. A 0.3 micron particulate filter completes the air purification process. The pure dry air is regulated down to 15 to 40 psig by instrument regulators and distributed to the gas, solvent and humidity modules at flow rates of 1 to 20 slm (standard liters per minute).

## Air Control and Humidification Module

The output of the pure air system is fed to an air control and humidification module. Widely varying water vapor concentrations are generated by precisely controlling the ratio of a "dry flow" that bypasses the humidity chamber and a "wet flow" that is saturated at 100% relative humidity while passing through a water vaporization chamber. The dry and wet flows are accurately controlled by mass flow controllers. The result is a carrier stream with known flow rate and humidity.

The water vaporization chamber uses an ultrasonic transducer to create a fog, and a 200 micron polypropylene filter to remove airborne droplets. A computer-actuated refill system maintains a constant liquid water level so the system can be used during very long experiments without "running dry". To avoid downstream condensation, the temperature of the water in the vaporizer is kept slightly below room temperature by electronically controlled Peltier coolers. The water temperature is measured in real time by the embedded digital electronic controller to allow precise calculation and control of the amount of water being delivered to the output stream.

The output stream of humidified carrier air is combined with the outputs of the gas and solvent modules and delivered to the test chamber as described below.

### Solvent Delivery Module

The solvent delivery module simultaneously delivers up to 8 solvents over a concentration range of approximately 1 ppm to 2500 ppm. An embedded computer actuates solenoid valves and performs real-time monitoring of inlet pressure and headspace temperature to achieve highly accurate solvent delivery.

Liquid solvent is stored in a corrosion-resistant glass jar capped by an anodized aluminum lid with an o-ring seal. A spun glass coalescing filter mounted on the inner face of the lid removes solvent droplets, and a thermistor mounted next to the coalescing filter measures the temperature of the solvent to facilitate accurate calculation of the solvent vapor pressure. A valve/restrictor assembly is manifold-mounted to the outside of the solvent jar lid to control air flow through the jar. A water bath surrounds the base of the jars to moderate the effects of changing ambient temperature, and the 8-jar assembly is connected using Teflon tubing to maintain the purity of the solvent-laden output flow.

On each jar, two sintered stainless steel restrictors establish parallel flows of 250 sccm (standard cubic centimeters per minute) and 5 sccm through each jar that is in use. The embedded digital controller pulse width modulates each of two solenoid valves on each jar (one for each restriction device) to control the fraction of the pure air flow that passes through the solvent jar to pick up solvent-vapor-laden air. The "high flow" restrictor allows up to 250 sccm of air to flow through a stainless steel bubbler immersed in liquid solvent, while the "low flow" restrictor controls up to 5 sccm of air that passes through the saturated headspace above the liquid. As the solvent-laden air exits the solvent jar, a spun glass coalescing filter removes entrained droplets. The solvent-laden air is immediately mixed with additional dry air to reduce the solvent vapor pressure and prevent downstream condensation. The output flows of the solvent jars are manifolded together and combined with the humidified carrier air entering the test chamber.

The temperature in the solvent jar headspace is measured in real time by a thermistor mounted near the coalescing filter. The embedded controller is programmed with a library of physical constants that characterize the vapor pressures of the available solvents as a function of temperature. Consequently, the computer can calculate and control the amount of solvent delivered to the output in real time. High level control software allows a user to simply request a concentration of an available solvent.

## Gas Delivery Module

The gas delivery module provides precise quantities of 3 independently controlled gases over a concentration range spanning 1-10,000 ppm in 10 slm of air. Gas flows are set by small stainless steel or glass restrictor tubes operated at 15 psi differential pressure. Gas leaving the restrictor tubes is combined with a 1.2 slm carrier flow of pure dry air to create small concentrations. The three gases are blended together in a dual-chamber gas mixing chamber providing residence times of 20 seconds and 1 minute prior to being manifolded into a higher flow rate (10 slm) output stream of humidified carrier air and delivered to the test chamber. Three restrictor tubes for each gas provide full scale flow ranges of 0.1, 3, and 100 sccm, corresponding to concentrations of approximately 10, 300, and 10,000 ppm in 10 slm of air. To provide delivery of a fraction of the maximum flow, the gas flow is pulse width modulated by solenoid valves under computer control. A 100:1 turndown on each of the ranges enables the creation of concentrations spanning 1 ppm to 10,000 ppm in 10 slm of air.

## Control Console and User Interface

The computer control console integrates and coordinates all of the modular functions of the gas delivery apparatus. Its user-friendly experimental design interface facilitates the specification and execution of repeatable experiments involving the delivery of complex mixtures of gases and solvents at well controlled humidities.

## Gas Delivery Verification System

An on-line gas delivery verification apparatus assures the accuracy of the delivered gas concentrations. A gas chromatograph (GC) is calibrated using purchased NIST-traceable gas standards. The calibrated GC then samples the output from the test station to verify the concentrations and purity of the delivered gases and vapors. A humidity meter calibrated with saturated salt solutions enables periodic verification of delivered water vapor concentration. This apparatus facilitates interpolation between gas standards and enables frequent verification of the test station's accuracy.

## Future Enhancements to the Gas Delivery Apparatus

The CO Test Protocol Report<sup>1</sup> prepared by the contractor for GRI describes a comprehensive CO test suite and presents a statistical analysis that shows that batches of at least 100 detectors must be tested at a time to establish statistically significant measures of reliability. To guarantee stable and well controlled gas mixtures to a test chamber containing 100 detectors, a gas blending apparatus that can operate at flow rates of approximately 100 liters per minute is required.

Mosaic Industries has developed new approaches to gas delivery that could be applied to the development of this advanced equipment in a future project. Such a project would result in the development of modular, appliance-style high performance gas blending equipment that could be used by sensor and detector manufacturers as well as test laboratories to perform automated testing of a wide variety of gas detection instruments.



## Task Itemization

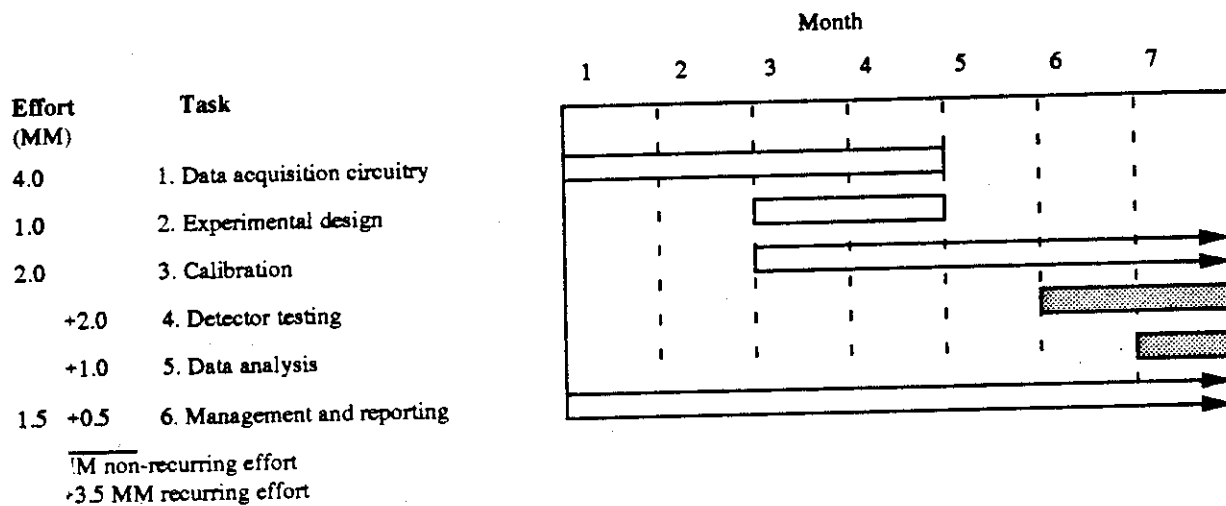
The following task itemization describes the work that must be performed to implement the proposed batch testing of CO detector instruments, and presents estimates of the required level of effort expressed in man months (MM).

1. Design, Build and Program the Data Acquisition Apparatus (4.0 MM)  
A data acquisition system must be designed and built to electronically detect and record the responses of the alarm instruments to the delivered gases and vapors. Circuitry will be designed, built, tested and installed in the test chamber so that the audible output of each alarm instrument can be detected, multiplexed and recorded by a local computer. The recorded data is then forwarded over a multi-drop serial communications link to the master computer where it is correlated with the gas delivery information.
2. Design the Experimental Protocols to Implement the CO Performance Tests (1.0 MM)  
The performance tests will be parsed into a set of discrete experiments to be run on separate days. Automated scripts will be designed to implement each test in the suite. Fits to the exponential dilution characteristics of the dynamic flow system will be performed to achieve the specified concentration-time products in the experiments. Levels of the target and interfering gases will be specified, and redundant gas delivery data points will be built in to check the repeatability of the response data within the experiments.
3. Calibrate the Gas Delivery System (2.0 MM)  
A GC and humidity measurement instrument will be used to initially calibrate and periodically recalibrate the delivered concentrations of the gases, vapors and humidities with respect to appropriate gas, solvent vapor and saturated salt humidity standards.
4. Perform the Specified Tests (2.0 MM per consortium member)  
The tests detailed in the Technical Approach section above will be performed using the gas delivery system. These tests will determine the responses of the instruments with respect to:
  - CO alarm levels at all of the specified time-dependent thresholds;
  - immunity to false alarms at low CO concentrations;
  - immunity to transient concentrations of CO;
  - repeatability of the alarm threshold tests; and,
  - immunity to false alarms with respect to interfering gases and vapors.

Each non-GRI consortium member may specify up to 10 detectors for batch testing. GRI may specify 5 detectors to be tested for each additional member in the consortium.
5. Data Analysis (1.0 MM per consortium member)  
The data collected in Task 4 will be graphed and statistically analyzed, and the results will be cogently summarized.
6. Project Management and Reporting (1.5 MM + 0.5 MM per consortium member)  
The manpower and material resources involved in the project will be managed. Monthly progress reports detailing the status of the project will be written and forwarded to the project manager. A comprehensive final report will be written to summarize the project results.

## Schedule and Manpower Requirements

Figure 2 is a timeline for the proposed research. The proposed start date for the project is July 1, 1996. The estimated project duration is 5 months plus 2 months for each additional non-GRI consortium member. Note that both the schedule and the manpower requirements depend on the number of consortium members, as this determines the total number of detectors that will be tested.



**Figure 2.** Task timeline of the proposed project. The effort summary is split into 2 columns representing non-recurring (GRI-supported) efforts and recurring (consortium-member-supported) efforts. The timeline bars for the recurring efforts are shaded. For simplicity, this figure presents the timeline assuming only one consortium member; in actuality, two additional calendar months are dedicated to each consortium member.

The following two tables summarize the manpower requirements for the proposed tasks. The "non-recurring efforts" to be supported by GRI are considered to be essentially independent of the number of consortium members. The "efforts for each additional consortium member" involve testing, analysis, and reporting related to a member-specified batch of up to 10 detectors, and these efforts are supported by the additional consortium members.

Task summary of non-recurring efforts:

<u>Task#</u>	<u>Description</u>	<u>Effort (man months)</u>
1.	Design and Build Data Acquisition Apparatus	4.0
2.	Design Experimental Protocols	1.0
3.	Calibrate the Gas Delivery System	2.0
6.	Project Management and Reporting	<u>1.5</u>
Subtotal: man months non-recurring effort		8.5

Task summary of efforts for each additional consortium member and associated detector batch:

<u>Task#</u>	<u>Description</u>	<u>Effort (man months)</u>
4.	Perform the Specified Tests	2.0
5.	Data Analysis	1.0
6.	Project Management and Reporting	<u>0.5</u>
Subtotal: man months additional effort per consortium member		3.5

Summary of required effort: 8.5 MM + 3.5 MM per additional consortium member

# Test Protocols for Carbon Monoxide Alarms Phase 1

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1. Goal is to provide a framework for understanding the technical determinants of the reported poor reliability of currently installed CO detectors.
2. The reliability of commercially available CO detectors is examined in light of the strengths and weaknesses of the sensing technologies they use and the potential influence of indoor environmental pollutants on their long term stability.
3. Performance tests are suggested which, if implemented as part of a comprehensive program of detector certification and manufacturing quality assurance, may contribute to improving the reliability of detectors installed in the future.

# The Field Performance of Currently Installed CO Detectors

- The "noisy" problem: high false alarm rates.

For most alarm calls in which residents did not ventilate the residence, responders measured insignificant CO concentrations.\*

Fraction of alarms	CO Concentration (Indoor - Outdoor)
1.7 %	> 99 ppm
8 %	> 35 ppm
92 %	< 36 ppm
73 %	< 10 ppm
54 %	< 5 ppm
30 %	0 ppm

- The "silent" problem: likely high rate of false negatives.

Colorimetric and Semiconductor sensors drift equally to greater and lesser sensitivities making false negatives about as likely as false alarms.

Electrochemical sensors generally drift more slowly but toward lesser sensitivity *eventually* making false negatives more likely than false alarms.

ex 100 ppm  
may after  
3 years  
go off  
at 300 or 30  
- Tokyo  
gas  
data  
Mos sensor  
can drift  
both wa

\* "Carbon Monoxide Response Survey Analyses: Suburban Chicago Data -- Interim Report", Resource Strategies, Inc., October 1995, GRI-95/0335

# Technical Determinants of the Performance of CO Detectors

## Outgoing Product Quality:

- Sensor variability
- Calibration difficulty
- Inadequate manufacturing quality control

## Field Reliability:

- Positive interferences
- Negative interferences
- Intrinsic drift
- Temperature/humidity variation
- Long term exposure to environmental poisons

To varying degrees the sensor technologies used, colorimetric, semiconductor, and electrochemical cell, suffer from drift, irreproducible fabrication, low production yield, and poor lifetime.

Sensor Technology			
	Semiconductor	Colorimetric	Electrochemical
Positive Interferences	Hydrogen, Alcohols, Aldehydes, and Ketones strongly interfere	Unsaturated hydrocarbons (C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>4</sub> H <sub>9</sub> ) Thiols (hydrogen sulfide) may strongly interfere	Hydrogen, Ethylene, Hydrogen sulfide, SO <sub>2</sub> , NO, and HCN weakly interfere
Negative Interferences	Ozone, NO <sub>x</sub> , and Chlorinated hydrocarbons may strongly interfere	Ozone, NO <sub>x</sub> , Ammonia, Halogens, Organic oxidants, and Chlorine?	Ozone and NO <sub>2</sub> may weakly interfere
Poisons	Thiols (hydrogen sulfide), Organometallics, Chlorinated hydrocarbons, SO <sub>2</sub> , Chlorine	Thiols (hydrogen sulfide), Unsaturated hydrocarbons, Ammonia, Chlorine	Thiols (hydrogen sulfide), Chlorinated hydrocarbons, Chlorine

## **Environmental Factors that May Compromise Detector Reliability:**

- Temperature
- Humidity
- Cumulative loadings of environmental pollutants and poisoning agents, including:
  - Ammonia,
  - Acetic acid,
  - H<sub>2</sub>S and other thiols,
  - Sulfur dioxide,
  - Ethanol,
  - Olefins,
  - Nitrogen oxides,
  - HCl,
  - Halogenated hydrocarbons,
  - Chlorine and others.

Common Household Pollutants That May Influence CO Detectors.		
Class	Examples	Sources
Aliphatic Hydrocarbons	Methane, Ethane, Propane, Butane, Hexane and Cyclohexane, Heptane, Octane, Nonane, Decane, Ethylene.	Fuel gases, propellants, liquid fuels including gasoline and kerosene, solvent cleaners, adhesives.
Amines	Ammonia, Mono-, Di-, and Tri-ethanolamine.	Household cleaners, cosmetics, shampoos, microbial sources.
Aromatic Hydrocarbons	Benzene, Phenol, Toluene, Xylene, Polynuclear aromatics (PNAs).	Cleaners, lacquers, enamels, smoke, cosmetics, gasoline and kerosene.
Halogenated Hydrocarbons	Methylene chloride, Freons and other CFCs, Carbon Tetrachloride, Trichloroethane, Paradichlorobenzene.	Refrigeration gases, adhesives, solvents, paints, cleaners, paint strippers, insecticides, plastic cements, mothballs.
Inorganic Gases	Ammonia, Chlorine, Ozone, Combustion Products: NO/NO <sub>2</sub> , SO <sub>2</sub> , CO <sub>2</sub> , Hydrogen, Hydrogen chloride, Hydrogen cyanide, Hydrogen peroxide, Phosphoric acid.	Household cleaners and laundry activities, combustion processes, external air (smog), copying machines, electrostatic air cleaners, cosmetics, wood, gas, and oil furnaces, kerosene heaters, external sources of combustion (e.g. auto exhaust), cigarette smoke, microbial sources, adhesives, paints, cat litter.
Organometallics	Silicone vapors, Tetra ethyl lead, Organophosphates.	Adhesives, lubricants, sealants, hair spray, leather cleaner, gasoline additives, insecticides, plasticizers, water-proofing materials.
Outdoor CO	CO -	Infiltration of motor vehicle exhaust, outdoor burning.
Partially Oxidized Hydrocarbons (alcohols, aldehydes, ketones, and carboxylic acids)	Methanol, Ethanol, Isopropanol, Formaldehyde, Acetaldehyde, Propionaldehyde, Acetone, Methyl ethyl ketone, Ethyl- and butyl-acetate, Benzophenone (diphenylketone), Butoxyethanol, Acetic acid.	Food preparation, nail enamels, alcoholic beverages, paints, building materials, cosmetics, fabric sizing (formaldehyde), fragrances, insecticides, kitchen and bathroom cleaners, vinegar, adhesives, cleaning solvents.
Thiols	Hydrogen Sulfide, Mercaptans.	External air, natural gas odorants, microbial sources.
VOCs	Volatilized oils, Higher molecular weight tars.	Cooking, auto exhaust, cigarette smoke, outgassing plastics.



**Table 3.3 Measurements of Indoor Pollutants**

Pollutant	Concentration *	Location/Condition	Reference
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**Aliphatic Hydrocarbons**

Methane	2 ppm	Atmospheric air	[61]
n-Pentane	0.46 - 3.88, 2.5 ppb	range and geo mean in office bldgs	[62]
n-Dodecane	0.44 - 23.8, 1.5 ppb	range and geo mean in office bldgs	[62]

**Aromatic Hydrocarbons**

Benzene	0 - 3 - 11 ppb 0.63 , 4.3 ppb 1.55 , 6.04 ppb	Homes, 48 hr avg US Homes, mostly California 2 wk outdoor mean in cities	[50] [63] [60] pg 50
Phenol	4.6 ppb	Typical conc. in lecture hall	[60] pg 73
Toluene (methylbenzene)	0 - 10 - 36 ppb 3.11 , 11.72 ppb 0.58 - 16.6, 2.6 ppb	Homes, 48 hr avg 2 wk outdoor mean in cities range and geo mean in office bldgs	[50] [60] pg 50 [62]
Xylene (dimethylbenzene)	1.2 , 8.4 ppb 2.28 , 6.54 ppb	US Homes, mostly California 2 wk outdoor mean in cities	[63] [60] pg 50
Trimethylbenzene	2.14 , 2.26 ppb	2 wk outdoor mean in cities	[60] pg 50

**Halogenated Hydrocarbons**

Methyl chloride	1.07 , 3.0 ppb	2 wk mean in cities	[60] pg 50
Methylene Chloride	0.5 ppb 0.42 , 3.75 pph 0.05 - 41.2, 0.4 ppb	Outdoor estimate 2 wk outdoor mean in cities range and geo mean in office bldgs	[64] [60] pg 50 [62]
Carbon Tetrachloride	0.075 , 0.135 ppb 0.17 , 0.28 ppb	US Homes, mostly California 2 wk outdoor mean in cities	[63] [60] pg 50
1, 2-Dichloroethane	0.08 , 0.52 ppb	2 wk outdoor mean in cities	[60] pg 50
Trichloroethane	0.52 , 4.5 ppb 0.29 , 1.03 ppb 0.08 - 72.4, 4.45 ppb	US Homes, mostly California 2 wk outdoor mean in cities range and geo mean in office bldgs	[63] [60] pg 50 [62]
Trichloroethylene	0.05 , 0.194 ppb 0.19 , 0.48 ppb 0.23 - 6.9, 1.8 ppb	US Homes, mostly California 2 wk outdoor mean in cities range and geo mean in office bldgs	[63] [60] pg 50 [62]
Tetrachloroethylene	0.042 , 1.16 ppb 0.31 , 1.48 ppb	US Homes, mostly California 2 wk outdoor mean in cities	[63] [60] pg 50
m/p-Dichlorobenzene	0.08 , 0.4 ppb	US Homes, mostly California	[63]

**Inorganic Gases**

Hydrogen	0.5 ppm	Atmospheric air	[61]
Hydrogen Cyanide	56 ppb	Room polluted with cigarette smoke	[60] pg 90
Nitric Oxide	1.05 ppm	Room polluted with cigarette smoke	[60] pg 90
Nitrogen Dioxide	0.005 - 0.11 ppm 0.005 - 0.317 ppm 0.020 , 0.066 ppm 0 - 0.025 - 0.177 ppm 0.2 ppm	US homes w/gas stoves English homes w/gas cookers 1979 median outdoor conc. in cities Homes, 48 hr avg Room polluted with cigarette smoke	[60] pg 2 [60] pg 2 [60] pg 47 [50] [60] pg 90
Sulfur Dioxide	8 , 37 ppb	Yearly averages in Chicago and NY	[65] pg 35
Carbon monoxide	2.04 +/- 2.55 ppm 2.5 - 28 ppm 3.1 - 7.8 ppm 1 , 5 ppm 0 - 3 - 27 ppm 0 - 3 - 22 ppm 20 ppm	US homes Offices, restaurants, bars, arenas Home kitchens w/gas stoves 1979 median outdoor conc. in cities Max 1 Hr avg outdoor conc. Max 1 Hr avg indoor conc. Room polluted with cigarette smoke	[66] [60] pg 2 [60] pg 2 [60] pg 47 [50] [50] [60] pg 90
Carbon dioxide	860 ppm 600 - 2500 ppm 9000 ppm	Lecture hall School room Nuclear submarines	[60] pg 2 [60] pg 2 [60] pg 2

**Table 3.3 Measurements of Indoor Pollutants (continued)**

Pollutant	Concentration <sup>a</sup>	Location/Condition	Reference
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**Inorganic Gases (cont.)**

Ozone	<0.002 - 0.068 ppm	Photocopying room	[60] pg 2
	<0.002 - 0.018 ppm	Homes w/electrostatic aircleaner	[60] pg 2
	0.007 , 0.060 ppm	1979 median outdoor conc. in cities	[60] pg 47
	0 - 0.7 ppm	Using an electronic air cleaner	[62]

**Partially Oxidized Hydrocarbons**

Methanol	55 ppb	Typical conc. in lecture hall	[60] pg 73
Ethanol	0.006 - 0.127 ppm	Office buildings	[62]
	0.023 ppm	Typical conc. in lecture hall	[60] pg 73
Isopropanol	0.001 - 0.062 ppm	Office buildings	[62]
2-Butoxyethanol	.035 - 4.8 ppb	Office buildings	[62]
Formaldehyde	0 - 0.05 - 0.33 ppm	Homes, 48 hr avg	[50]
	0.06 - 0.46 - 1.67 ppm	Homes w/chipboard walls	[60] pg 2
	0.03 - 1.77 ppm	Mobile homes	[60] pg 2
	0.590 ppm	Room polluted with cigarette smoke	[60] pg 90
Acetaldehyde	4.2 ppb	Typical conc. in lecture hall	[60] pg 73
	370 ppb	Room polluted with cigarette smoke	[60] pg 90
Total Aldehyde	0.02 - 0.88 - 4.2 ppm	Mobile homes registering complaints in Wisconsin	[67] pg 64
Acetone	20.6 ppb	Typical conc. in lecture hall	[60] pg 73
	2.7 - 11.6 ppb	Office Bldgs	[62]
Diethylketone	5.7 ppb	Typical conc. in lecture hall	[60] pg 73
Acetic acid	9.9 ppb	Typical conc. in lecture hall	[60] pg 73
Butyric acid	15.1 ppb	Typical conc. in lecture hall	[60] pg 73

**VOCs**

Nonmethane VOCs	227 - 6,972 $\mu\text{g}/\text{m}^3$ avg 592 $\mu\text{g}/\text{m}^3$ (0.29 ppm ethanol equivalents)	12 nonsmoking office bldgs.	[52]
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<sup>a</sup> Where otherwise unspecified, single values represent time averaged mean concentrations and multiple values represent sets of either (low concentration - high concentration), (low - mean or median - high), or (low median, high median) values of a distribution among different sites of time averaged concentrations.

**Table 3.4 Indoor Pollutant Emissions from Cigarettes**

Pollutant	Emission Rate <sup>a</sup> (mg per cigarette)	Concentration <sup>b</sup>
<b>Condensing Particulates</b>		
Tar	37.	363. $\mu\text{g}/\text{m}^3$
Nicotine	6.	59. $\mu\text{g}/\text{m}^3$
Total Phenols	0.8	7.9 $\mu\text{g}/\text{m}^3$
<b>Gases and VOCs</b>		
Ammonia	76.	983. ppb
Acetone	1.2	4.5 ppb
Formaldehyde	1.3	9.5 ppb
Acetaldehyde	2.3	8.7 ppb
Methylchloride	2.	8.7 ppb
CO	48.	376. ppb
CO <sub>2</sub>	360.	1.8 ppm
HCN	0.54	4.4 ppb
NO	2.6	19. ppb
NO <sub>2</sub>	0.64	3. ppb

- a Sum of the middle of the range sidestream and mainstream emissions, as quoted by [60] Table 4.5.
- b Computed as an averaged indoor concentration assuming 2 packs or 40 cigarettes burned per day into a volume of 340 m<sup>3</sup> (a 1500 sq. ft. home) with complete air exchange every 2 hours.

**Table 3.5 Emissions of Indoor Pollutants by Sedentary Persons**

Pollutant	Emission Rate <sup>a</sup> (mg/day per person)	Concentration <sup>b</sup>
Ammonia	32.	41. ppb
Phenol	9.1	2.1 ppb
Toluene	7.7	1.8 ppb
Acetone	70.	27. ppb
Acetaldehyde	7.4	2.8 ppb
Diethylketone	16.	4.1 ppb
Ethyl acetate	19.	4.7 ppb
Acetic acid	23.	8.4 ppb
Butyric acid	52.	13. ppb
Amyl alcohol	21.	5.2 ppb
Methanol	66.	45. ppb
Ethanol	77.	37. ppb
Carbon monoxide	4840.	3.8 ppm
Carbon dioxide	786,000.	392. ppm
Hydrogen sulfide	2.9	1.9 ppb

- a Average of emission rates in lecture classes and exams by students, as quoted by [60] Table 4.16. This emission rate roughly corresponds to a metabolic activity level of 1 Met (50 kcal/hr-m<sup>2</sup>) for a person of 2 m<sup>2</sup>.
- b Averaged indoor concentration assuming an average of 4 persons present in a 1500 sq ft home (340 m<sup>3</sup>), a metabolic level of 1 Met, and an indoor air residence time of 2 hrs.

**Table 3.6 Indoor Pollutants Resulting from the Use of Household Chemicals**

Gaseous Pollutant	Source	Fraction in Source	Quantity Volatilized	Dose per Incident	Frequency of Use	Average Concentration
Acetic acid	Vinegar	5 %	30 ml	29 ppm-hr	3/week	518 ppb
Acetone	Nail polish remover	100 %	10 ml	153 ppm-hr	2/month	420 ppb
Ammonia	Household ammonia	5 %	15 ml	50 ppm-hr	2/week	595 ppb
Chlorine <sup>a</sup>	Laundry Bleach	2.5 %	5 ml	2 ppm-hr	2/week	24 ppb
p-Dichlorobenzene <sup>b</sup>	Mothballs	100 %	9 mg/hr	continuous exposure		69 ppb
Ethanol	Alcoholic beverages	15 %	15 ml	121 ppm-hr	2/month	332 ppb
HMDS <sup>c</sup>	Oils, lubricants	trace	1.3 mg/hr	continuous exposure		9 ppb
Hydrochloric acid	Bathroom cleaner	2 %	30 ml	22 ppm-hr	1/week	131 ppb
Isopropanol	Rubbing alcohol	70 %	15 ml	154 ppm-hr	2/month	422 ppb
Methylethylketone (MEK)	Uncapped marker pen or plastic adhesive	50-100 %	2 ml	26 ppm-hr	1/month	36 ppb
Trichloroethane	Typewriter correction fluid	50-80 %	0.25 ml	3 ppm-hr	1/day	126 ppb

- We assume that the chlorine bleach comprises a 5.25 wt-% solution of sodium hypochlorite, or 2.5 wt-% chlorine, that appx. 50 ml is used per wash and that 10% of that either volatilizes or decomposes in hot water eventually releasing chlorine.
- For paradichlorobenzene originating from mothballs we measured a rate of sublimation in the laboratory at room temperature of 150 gm over a two year period from a closed, resealed container, or approximately 9 mg/hr. It is likely that any residential use of moth balls will result in a much greater sublimation rate than this.
- It is not known what concentrations of organosilicones might be found indoors. However, a standard test for the poison resistance of catalytic bead sensors is to expose them to 10 ppm hexamethyldisilozane (HMDS) and measure the drop off in their methane sensitivity up to a total dose of 250 ppm-hr. Modern catalytic bead sensors should last at least one day before there is any significant poisoning. Nevertheless, these same sensors in industrial settings are often poisoned by silicones, limiting their lifetimes to months or even weeks. So, a dose level near the upper end of this range is chosen: 9 ppb over 3 years, 10 ppm-day, or 240 ppm-hr.

# Maximum Likely Sensor Lifetime Exposures for Various Indoor Pollutants

Pollutant	EPA Outdoor Standard <sup>a</sup>	ACGIH <sup>b</sup> or NIOSH PEL	ASHRAE Indoor Design Standard <sup>c</sup>	Maximum <sup>d</sup> Likely Mean Indoor Concentration	Lifetime Exposure (ppm-days) <sup>e</sup>
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## Aliphatic Hydrocarbons

Methane				2000. ppb	2190.
n-Pentane				9. ppb	10.
n-Dodecane				24. ppb	26.

## Amines

Ammonia		25 ppm	.66 / 9.2 ppm	983. ppb	1076.
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## Aromatic Hydrocarbons

Benzene		10 ppm		11. ppb	12.
Phenol				5. ppb	5.5
Toluene		100 ppm		36. ppb	39.
Xylene		100 ppm		8.4 ppb	9.2
Trimethylbenzene				2.3 ppb	2.5

## Halogenated Hydrocarbons

Methyl chloride		50 ppm		3. ppb	3.3
Methylene chloride		100 ppm	13.6 / 41 ppm	41. ppb	45.
Carbon tetrachloride		5 ppm		0.3 ppb	0.32
Dichloroethane		200 ppm	47 / 1.4 ppm	0.5 ppb	0.55
Trichloroethane		50 ppm		126. ppb	138.
Trichloroethylene		50 ppm	.88 / 2.88 ppm	6.9 ppb	7.5
Tetrachloroethylene		50 ppm		1.5 ppb	1.6
m/p-Dichlorobenzene		75 ppm		69 ppb	76

## Inorganic Gases

Carbon Dioxide		5000 ppm	5000 ppm	1000 ppm	1.1 x 10 <sup>6</sup>
Carbon Monoxide	9 ppm average 35 ppm 1 hr.	50 ppm		2 ppm	2200.
Chlorine		1 ppm	.032 / .1 ppm	24. ppb	26.
Hydrogen				500. ppb	548.
Hydrogen chloride		5 ppm ceil	.25 / 2 ppm	131. ppb	143.
Hydrogen cyanide				56. ppb	61.
Nitric oxide		25 ppm		1000. ppb	1095.
Nitrogen dioxide	0.05 ppm avg once/year	3 ppm		200. ppb	219.
Ozone	0.12 ppm once/year	0.1 ppm		60. ppb	66.
Sulfur dioxide	0.03 ppm avg 0.14 ppm 24hr	2 ppm		37. ppb	41.

## Organometallics

HMDS				9. ppb	10.
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## Partially Oxidized Hydrocarbons

Methanol		200 ppm	1 / 3 ppm	55. ppb	60.
Ethanol				332. ppb	364.
Isopropanol				422. ppb	462.
2-Butoxyethanol				5. ppb	5.5
Formaldehyde		2 ppm	112 ppb	590. ppb	646.
Acetaldehyde		100 ppm		370. ppb	405.
Total aldehyde				880. ppb	963.
Acetone		750 ppm	2.7 / 9.3 ppm	420. ppb	460.
Diethylketone				6. ppb	7.
Methyl ethylketone		200 ppm		36. ppb	39.
Acetic acid		100 ppm		518. ppb	567.
Butyric acid				15. ppb	16.

## Thiols

Hydrogen sulfide		10 ppm	26 - 33 ppb	30. ppb	33.
Methyl mercaptan		0.5 ppm			
Butyl mercaptan		0.5 ppm			

## VOCs

Non-methane HCs	0.24 ppm, 3 hr once/vr			290. ppb as ethanol equiv.	318.
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- a. EPA regulations in 1971, 1978, and 1979.
- b. As a time weighted averaged threshold limit value.
- c. As permissible long term (24 hr) / short term (30 min) exposures. Indoor Design Standard taken from Table 7.1 of [60].
- d. For some common household pollutants the average concentrations listed in Table 3.6 are used. For other pollutants the greatest 48-hr average from a study of California residences, [50] as listed in Table 3.3, is used if available. Otherwise the greatest of the other "non-sick-building" citations for commercial buildings of Table 3.3 is used. If only "sick" commercial building citations are available, then the median value is used rather than the greatest, although this precaution may not be necessary; these "reputedly sick" buildings have shown no greater VOC levels than presumably healthy buildings [62]. For chlorine and H<sub>2</sub>S the ASHRAE indoor design standard concentrations are used, for ammonia the value of Table 3.4 is used.
- e. Assuming a requirement for a three year sensor lifetime.

## The Properties of Various Detection Methods

Sensor Property	Technology			
	MOS	Colorimetric	Electrochemical	Infrared
Long Term Stability	Good, if recalibrated	Poor	Adequate	Excellent
Short Term Stability	Poor, +/- 20%	Unknown	Very good, +/- 2%	Excellent
Lifetime	Very good, >5 years with recalibration	Unpredictable, exposure related. Not recalibratable.	Good 2-5 years	Excellent, >>5 years
Resolution	Poor (+/-20% after calibration)	Poor (+/-25% after manufacture) and uncalibratable	Very good (+/-2% after calibration)	Excellent, limited only by engineering design
Detection Range	10 ppm to 100%	500-50,000 ppm-min (integrating)	1-1000 ppm	Limited only by engineering design
Immunity to False Alarms	Poor to adequate	Reportedly poor	Adequate	Excellent
Immunity to False Negatives	Good throughout lifetime	Unknown	Good until end of lifetime	Excellent
Immunity to Poisoning	Good in the short term	Unknown but reportedly poor	Adequate with filter	Excellent
Response Type	Nonlinear but monotonic	Nearly linear	Linear	Linear
Sensitivity Drift	Moderate, partly progressive, exposure related, appx 1-5%/month	Unknown	Small but progressive, max 12% @6 months, 25% @5 yrs	Very little drift, limited only by engineering design
Zero Drift	Partly progressive, and exposure related	Unknown	Progressive, and temperature related	Theoretically small
Lifetime Extendibility	Lifetime indefinitely extendible by recalibration	Not extendible	Not extendible	Unlimited lifetime
Primary Failure	By progressive drift to greater and lesser sensitivities.	1/2 fail silently, 1/2 fail with false alarm.	Fails silently, with loss of sensitivity.	Electronics fails infrequently or optics becomes dirty
OEM Sensor Cost	Inexpensive \$5-10	Inexpensive <\$5	Inexpensive \$5-10	Expensive \$30-\$100
Primary Advantages	Cost, Lifetime, Durability	Cost, Simplicity	Accuracy	Reliability and Accuracy
Primary Disadvantages	Unselective, Inaccurate	Not Resettable, Uneven Quality	Lifetime, Cost	Cost

*slightly different from my draft copy based on data received & own exp. with MOS sensors*

*most widely studied*

# The Components of a Comprehensive Standard

To adequately assure the reliability of CO detectors a comprehensive standard must have functional components related to each phase of a detector's life cycle: its design, manufacture, and lifetime experience in the field. Quantitative estimates of required reliabilities (for the detector's effectiveness in mitigating hazards, time-of-manufacture failure rate, and end-of-lifetime failure rate) enter in different proportions as design parameters in each of these stages and determine the degree of compliance testing needed for each stage. The three functional components of a comprehensive standard are:

- **Design certification**

Specifies the reliability of the individual components of an alarm and certifies that all alarms are designed to meet a common operational specification, verified by one-time laboratory tests of a representative sample of manufactured units. The design standard focuses on two areas, the detector's operational specifications and the laboratory tests needed to certify them.

- **Manufacturing quality assurance**

Quality control and quality assurance procedures ensure that as alarms are manufactured they continue to comply with a uniform operational specification. This generally requires assembly line testing, ISO auditing, 100% product testing of key specifications, statistical sampling, and/or batch testing of manufactured units to ensure that they meet all performance and quality specifications. The purpose of this testing is to estimate the time-of-manufacture failure rate and to assure that it is below an agreed upon target rate.

- **Lifetime compliance**

In-house accelerated lifetime tests, outside field tests, and field sampling and testing are performed to ensure that instruments continue to meet their operational specification throughout their specified lifetime. A quantitative end-of-lifetime failure rate should form the basis of these tests. Published statistics justifying detector lifetime, though not yet available, would provide valuable reassurance to consumers about the continued functionality of their detectors.



# Steps in the Development of a Comprehensive Standard for CO Detectors

1. Develop a database of scientific and technical information concerning CO detectors, including:
  - the reliability of existing detectors;
  - an analysis of field data including installation rates and alarm response rates;
  - a retrospective analysis of the causes of detector failure;
  - the dose/response relationship for CO exposure;
  - the demographics of susceptibility to CO poisoning;
  - the indoor pollutants likely to compromise detector performance; and,
  - the cumulative pollutant doses found in residential settings.
2. Form a consensus for the fundamental scope and purpose of CO detectors.
3. Quantify minimum detector reliabilities appropriate to the residential market, including
  - a detector's effectiveness when working properly,
  - its outgoing product quality at the time of manufacture,
  - its lifetime reliability in the face of environmental pollutants,
  - and the confidence levels at which these reliabilities should be measured.
4. Develop a common operational specification for the performance of CO detectors.
5. Assure target reliabilities through a program of comprehensive quality management that includes components for
  - design certification,
  - manufacturing quality assurance, and
  - lifetime quality assurance.

## Comprehensive Tests for CO Detectors

**Target reliability:** Detectors must pass Tests 1-6 with a cumulative failure rate of less than 1% at a 90% confidence level. Detectors must pass Test 8 with a cumulative failure rate of less than 3.7% at a 90% confidence level.

Test Purpose	Test Method and Gases Used
<b>1. Alarm Level</b> Detectors should consistently alarm below a level that would produce 10% COHb in an exposed individual.	Detectors must alarm within 90 minutes on exposure to 100 ppm CO, within 35 minutes on exposure to 200 ppm and within 15 minutes on exposure to 400 ppm, at various ambient temperatures.
<b>2. Immunity to Low Concentrations</b> Detectors should not alarm on long term exposure to ambient CO levels.	Detectors must not alarm when continuously exposed to 20 ppm for a duration of 14 days.
<b>3. Surge Immunity</b> Detectors should not alarm in response to short duration exposures to CO levels that would produce less than 2% COHb in an exposed individual.	Detectors must not alarm when exposed to 50 ppm for 30 minutes.
<b>4. Distribution of Sensitivity</b> The intrabatch variation in detector sensitivity should be less than that which would produce a specified population failure rate for the alarm level test and low concentration immunity test at a specified confidence level.	A sufficiently large population of detectors must be subjected to the alarm level and low concentration immunity tests. Failure rates may be estimated from observed failure rates and/or extrapolated from the observed distribution of detector sensitivity.
<b>5. False Negatives</b> Detectors should not fail to alarm even in the presence of the maximum concentrations of oxidant gases expected to be found in homes.	Detectors must not fail the alarm level test while simultaneously being exposed to 1 ppm each of nitric oxide and chlorine.
<b>6. False Positives</b> Detectors should alarm in the presence of the maximum concentrations of reducing gases expected to be found in homes.	Detectors must not alarm in response to two hour exposures to the gases and concentrations of Table 6.2.
<b>7. Repeatability</b> Detectors should remain fully functional after having alarmed several times in response to CO.	Single detectors must pass all challenges of the alarm level test without replacement. They must also pass the alarm level test and the surge immunity test one day after a prior alarm test.
<b>8. Accelerated Lifetime Exposure Tests</b> Detectors should remain functional throughout their stated lifetime in a residential environment.	Detectors must pass Tests 1-6 after exposure to expected cumulative lifetime doses of the representative gases and concentrations of Table 6.3. The post-exposure cumulative failure rate for Tests 1-6 must be less than 3.7% at a 90% confidence level.

*Japanese standard says 30ppm*

*UL uses 60% confidence level in their tests*

How many units need to be tested to establish a failure rate at a given confidence level (CL)?

Upper and Lower Bounds on the Expected Number of Failures Given an Observed Number of Failures vs. Confidence Level						
Number of Failures Observed	Confidence Level (CL)					
	99%	95%	90%	80%	60%	50%
	2.33 s.d.	1.65 s.d.	1.28 s.d.	0.84 s.d.	0.25 s.d.	0.0 s.d.
0	4.6 / 0.0	3.0 / 0.0	2.3 / 0.0	1.6 / 0.0	0.9 / 0.0	0.7 / 0.0
1	6.6 / 0.01	4.7 / 0.05	3.9 / 0.11	3.0 / 0.22	2.1 / 0.5	1.7 / 0.7
2	8.4 / 0.21	6.3 / 0.36	5.3 / 0.53	4.3 / 0.82	3.1 / 1.4	2.7 / 1.7
3	10 / 0.44	7.8 / 0.82	6.7 / 1.1	5.5 / 1.5	4.2 / 2.3	3.7 / 2.7
5	13 / 1.3	11 / 2.0	9.3 / 2.4	7.9 / 3.1	6.3 / 4.2	5.7 / 4.7
10	20 / 4.1	17 / 5.4	15 / 6.2	14 / 7.3	12 / 8.9	10.7 / 9.7
20	33 / 11.1	29 / 13.3	27 / 14.5	25 / 16.2	22 / 18.6	20.7 / 19.7
50	69 / 35	63 / 39	60 / 41	57 / 44	52 / 47.9	50.7 / 49.7

Example:

Suppose we need to establish that a failure rate is less than 1% at a 90% confidence level. From the table, even if no failures are observed, at a 90% confidence level we can expect at most 2.3 failures. For this number of failures to correspond to 1% we would need to have tested 230 units.

Consequently, if we test 230 units without observing a failure then we can be 90% confident that the actual failure rate is less than 1%. That is, if we were to perform this test many times with different sets of 230 units, and if the actual failure rate were greater than 1%, then in at least 90% of our tests we would observe some failures. If in a test of 230 units we were to observe a single failure then we would have established that the actual failure rate is less than  $3.9/230$  or 1.7% at 90% CL. We also would have established a lower bound on the failure rate. Consulting the table, there is a 90% likelihood that for one observed failure the actual failure rate is greater than  $0.11/230=0.05\%$ . That is, if we were to perform this test many times with different sets of 230 units, and if the actual failure rate were less than 0.05%, then in at least 90% of our tests we would not observe any failures. In only 10% of the tests would we observe one or more failures.

Accelerated Lifetime Test Gases and Exposures		
Class	Test Gas	Exposure (ppm-days)
Alkanes	i-Butane	700.
Alkenes	Ethylene	350.
Amines	Ammonia	650.
Aromatics HCs	Toluene	70.
Halogenated HCs	Trichloroethane	200.
Alcohols	Ethanol	900.
Aldehydes	Formaldehyde	1000.
Ketones	Acetone	500.
Carboxylic Acids	Acetic acid	600.
Hydrogen	Hydrogen	550.
Mineral Acids	Hydrogen chloride	143.
	Sulfur dioxide	41.
Oxidants	Nitric oxide	1400.
	Chlorine	40.
Catalyst Poisons	Hexamethyldisiloxane	10.
Thiols	Hydrogen sulfide	33.

# Test Protocols for Carbon Monoxide Alarms

## Phase 2

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Newark, CA  
510-790-8222

1. Tests the performance of those commercially available CO detectors of most interest to consortium members. Tests include measurement of alarm level, surge immunity, repeatability, and immunity to interferences.
2. Starts with simple tests and adds progressively more demanding tests at the behest of consortium members.
3. Serves the needs of regulatory agencies, utilities, nationally recognized testing laboratories, detector manufacturers, and the public.

## UL 2034

The current standard, while it thoroughly and comprehensively specifies and tests the mechanical and electrical aspects of the detectors, does not as comprehensively test their gas-detecting performance, and provides no tests that assure their time-of-manufacture or lifetime reliabilities. As a result, the present standard does not provide sufficient assurance to the consumer that their detector actually works. That is, it does not assure the consumer that there will not be an unreasonable and costly number of false alarms, that the detector will not fail to alarm when it should, and that it will remain fully functional for its stated lifetime.

Needed:

- Explicit, rather than *ad hoc*, “margins-of-safety” for at-risk populations
- Realistic reliability goals
- Minimal lifetime requirement
- Clearly stated requirements for
  - Time-of-manufacture product quality
  - Calibration
  - Lifetime reliability
- More comprehensive performance tests including those for
  - Repeatability
  - Accelerated lifetime exposure

UL2034 assumes a much greater rate of CO absorption than found in the average residential occupant, and in particular, much faster dynamics of CO absorption/desorption than found in those whose pulmonary function is compromised by illness. UL2034 models at-risk subpopulations with COHb curves derived from a super-healthy subpopulation !

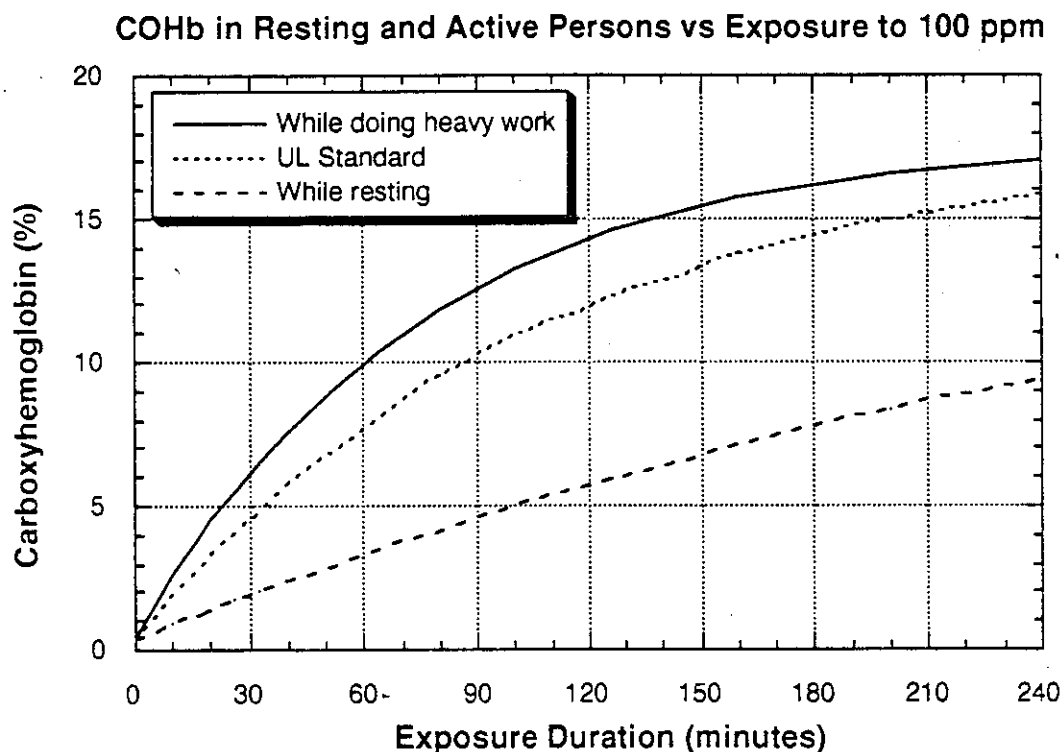


Figure 2.2 Relationship between the duration of exposure to 100 ppm CO and the level of carboxyhemoglobin in the blood for a person resting and engaged in vigorous activity. The intermediate curve represents the level of exertion assumed by UL 2034. The same mathematical model is used as in Figure 2.1 [33].

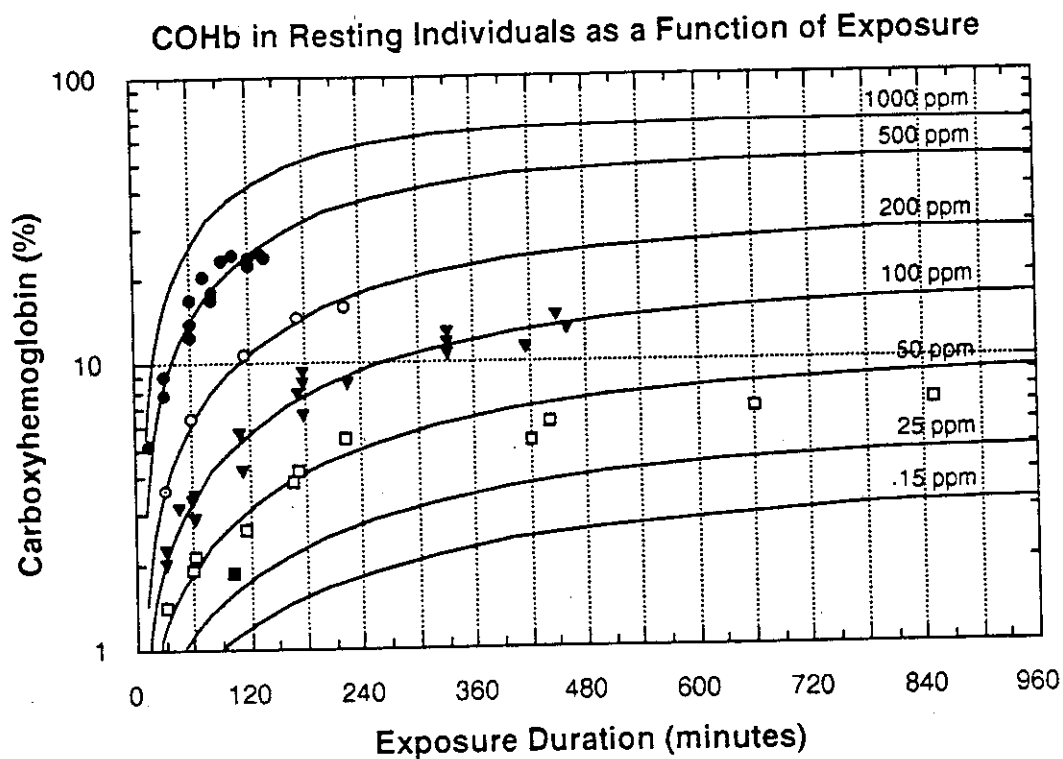


Figure 2.1 Relationship between duration of exposure, ambient CO concentration, and carboxyhemoglobin in the blood for a person at rest. The solid lines represent a mathematical model based on physiological principles and the markers represent measurements of blood COHb. Sources for the data and the computer simulations used are found in [33].



# CURRENT ACTIVITIES

ETL - <sup>in progress</sup>  
testing  
labs

- BASIC PERFORMANCE TESTS (COMPLETED)
- TEST PROTOCOL DEVELOPMENT -- PHASE I (COMPLETED)

- ASTM TASK FORCE ON TESTING (NEW)

run limited  
number of  
tests from GRI  
draft report, Gas  
utilizes in forested  
looking for other

- TEST PROTOCOL DEMONSTRATION -- PHASE II (NEW)

possibly  
implemented  
through IAS/NASA  
trying to  
highlight the specs  
up to gas industry to  
pursue

- GAS INDUSTRY TECHNICAL SPECIFICATION FOR CO DETECTORS (NEW)

**CO DETECTOR TESTING:  
DISCUSSION WITH CONSUMER  
PRODUCT SAFETY COMMISSION**

**MAY 14, 1996**

**TED A. WILLIAMS  
PRINCIPAL TECHNOLOGY MANAGER,  
GAS RESEARCH INSTITUTE  
CHICAGO, ILLINOIS**

**GRI**

# PROPOSED TESTS

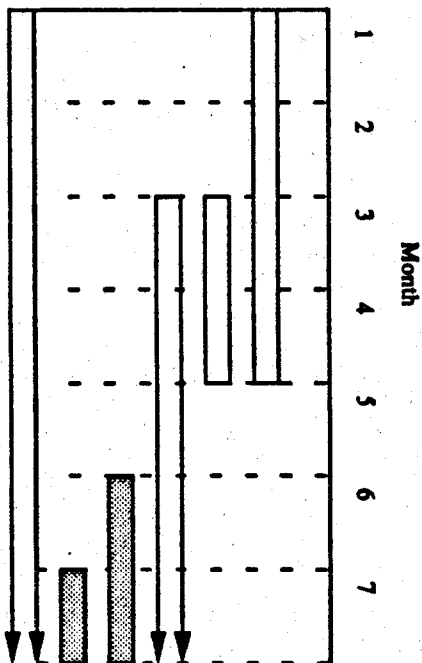
- SENSITIVITY TESTS (UL 2034)
- IMMUNITY TO LOW CONCENTRATIONS
- SURGE IMMUNITY TESTS
- REPEATABILITY TESTS
- INTERFERENCE TESTS

total  
is  
lacking  
UL 2034



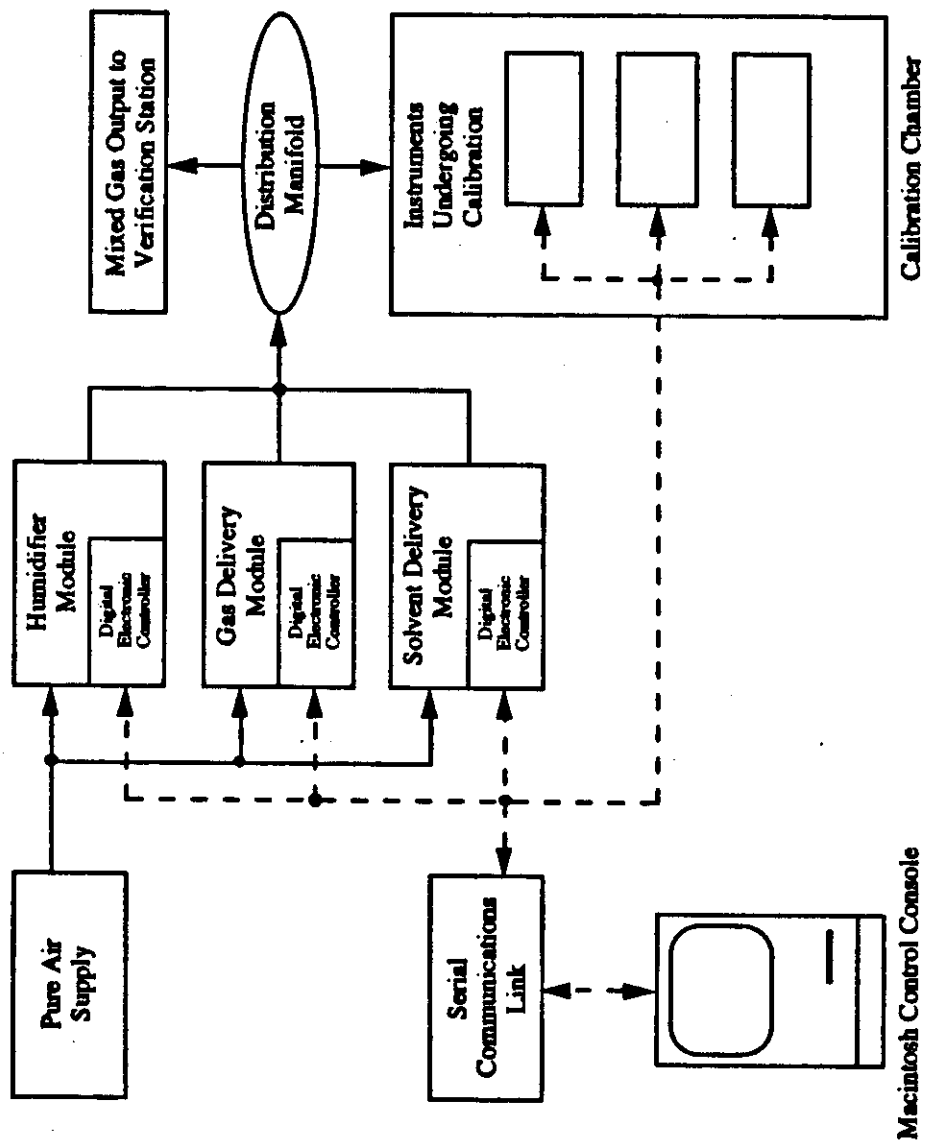
# TEST SCHEDULE

Effort (MM)	Task
4.0	1. Data acquisition circuitry
1.0	2. Experimental design
2.0	3. Calibration
+2.0	4. Detector testing
+1.0	5. Data analysis
1.5 +0.5	6. Management and reporting
<u>8.5 MM non-recurring effort</u>	
+3.5 MM recurring effort	



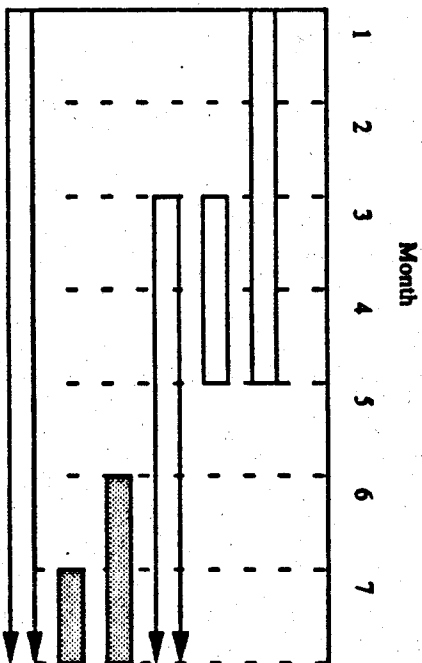
- good is to  
benchmark previous  
net performance of devices

# TEST FACILITIES



# TEST SCHEDULE

Effort (MM)	Task
4.0	1. Data acquisition circuitry
1.0	2. Experimental design
2.0	3. Calibration
+2.0	4. Detector testing
+1.0	5. Data analysis
1.5 +0.5	6. Management and reporting
<u>8.5 MM non-recurring effort</u>	
+3.5 MM recurring effort	



- good is to  
benchmark previous  
net performance of devices

# PROGRAM ORGANIZATION

- COSPONSOR ROLE

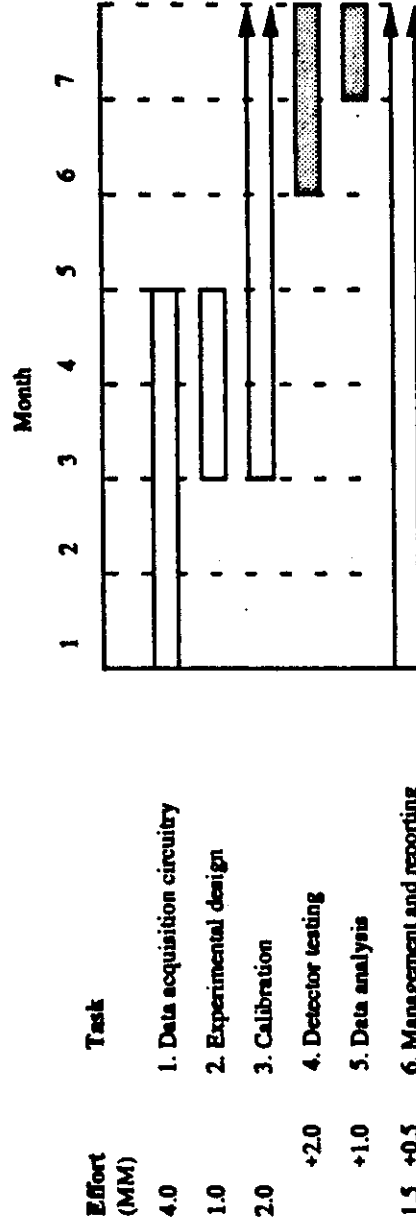
- GRI ROLE *to come up with funding*

- TIMETABLE FOR PARTICIPANT SOLICITATION

*start in  
early June  
or July*



# TEST SCHEDULE



goal is to  
- benchmark product & services  
- not performance of devices